

DEPARTMENT OF CONSUMER & INDUSTRY SERVICES

DIRECTOR'S OFFICE

OCCUPATIONAL HEALTH STANDARDS

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(By authority conferred on the director of the department of consumer and industry services by section 24 of
1974 PA 154, MCL 408.1024, and Executive Reorganization Order Nos. 1996-1 and 1996-2, MCL 330.3101 and
445.2001)

R 325.50074 of the Michigan Administrative Code is rescinded as follows:

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PART 303. METHYLENEDIANILINE (MDA)

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R 325.50051 Scope and application.

Rule 1. (1) These rules apply to all occupational exposures to methylenedianiline (MDA), chemical abstracts service registry no. 101-77-9, except as provided in subrules (2) to (6) of this rule. This application includes construction, alteration, repair, maintenance, and renovation activities that involve MDA. These rules also apply to the transportation, disposal, storage, containment, and spill cleanup of MDA at construction sites.

(2) Except as provided in subrule (7) of this rule and in R 325.50056(6), these rules do not apply to the processing, use, and handling of products that contain MDA if initial monitoring indicates that the product is not capable of releasing MDA in excess of the action level under the expected conditions of processing, use, and handling that will cause the greatest possible release and if dermal exposure to MDA, as defined in R 325.50052(f), cannot occur.

(3) Except as provided in subrule (7) of this rule, these rules do not apply to the processing, use, and

handling of products that contain MDA if objective data are reasonably relied upon that demonstrate that the product is not capable of releasing MDA under the expected conditions of processing, use, and handling which will cause the greatest possible release and if dermal exposure to MDA cannot occur.

(4) Except for the provisions of R 325.50054 and of 29 C.F.R. §1910.1200 cited in R 325.50064(1), these rules do not apply to the storage, transportation, distribution, or sale of MDA in intact containers that are sealed in a manner that contains the MDA dusts, vapors, or liquids.

(5) Except as provided in subrule (7) of this rule, these rules do not apply to materials in any form that contain less than 0.1% MDA by weight or volume.

(6) Except as provided in subrule (7) of this rule, these rules do not apply to finished articles that contain MDA, as defined in R 325.50052(j).

(7) Where products that contain MDA are exempted pursuant to the provisions of subrules (2) to (6) of this rule, an employer shall maintain records of the initial monitoring results or objective data supporting that exemption and the basis for the employer's reliance on the data, as provided in the recordkeeping provisions of R 325.50072.

R 325.50052 Definitions.

Rule 2. As used in these rules:

(a) "Act" means 1974 PA 154, MCL 408.1001 et seq.

(b) "Action level" means a concentration of airborne MDA of 5 parts MDA per billion parts of air (5 ppb) as an 8-hour, time-weighted average.

(c) "Authorized person" means any person who is specifically authorized by an employer to enter a regulated area, or any person who enters a regulated area as a designed representative of employees, for the purpose of exercising the right to observe monitoring and measuring procedures described in R 325.50073 or any other person who is authorized by the act or the administrative rules issued under the act.

(d) "Container" means any of the following, but does not include a pipe or piping systems:

- (i) A barrel.
- (ii) A bottle.
- (iii) A can.
- (iv) A cylinder.
- (v) A drum.
- (vi) A reaction vessel.
- (vii) A storage tank.
- (viii) Commercial packaging.

(e) "Decontamination area" means a work area which is outside of, but as near as practical to, a regulated area, which consists of a storage area, a wash area, and a clean change area, and which is used for the decontamination of workers, materials, and equipment that are contaminated with MDA.

(f) "Dermal exposure to MDA" means any employee exposure that involves skin contact with either of the following nonairborne forms of MDA:

(i) Liquid, powdered, granular, or flaked mixtures that contain MDA in concentrations greater than 0.1% by weight or volume.

(ii) Materials, other than finished articles, that contain MDA in concentrations greater than 0.1% by weight or volume.

(g) "Director" means the director of the Michigan department of consumer and industry services or his or her designee.

(h) "Emergency" means an occurrence, such as an equipment failure, a rupture of containers, or the failure of control equipment, that results in an unexpected and potentially hazardous release of MDA.

(i) "Employee exposure" means exposure to MDA that would occur if the employee were not using respirators or protective work clothing and equipment.

(j) "Finished article containing MDA" means a manufactured item for which all of the following provisions apply:

(i) The item is formed to a specific shape or design during manufacture.

(ii) The item has an end use function or functions that are dependent, in whole or part, upon the item's shape or design.

(iii) If applicable, the item is an item that is fully cured by having been subjected to the conditions of time and temperature necessary to complete the desired chemical reaction.

(k) "Historical monitoring data" means monitoring data for construction work that meet all of the following conditions:

(i) The data upon which judgments are based are scientifically sound and are collected using methods that are sufficiently accurate and precise.

(ii) The processes and work practices that were in use when the historical monitoring data were obtained are essentially the same as the processes and work practices to be used during the job for which initial monitoring will not be performed.

(iii) The characteristics of the MDA-containing material being handled when the historical monitoring data were obtained are the same as the characteristics of the MDA-containing material on the job for which initial monitoring will not be performed.

(iv) The environmental conditions that were prevailing when the historical monitoring data were obtained are the same as the environmental conditions on the job for which initial monitoring will not be performed.

(v) Other data that are relevant to the operations, materials, processing, or employee exposures covered by the exemptions from monitoring specified in R 325.50056(1)(a) and (b) are substantially similar. The data shall be scientifically sound, the characteristics of the MDA-containing material shall be similar, and the environmental conditions shall be comparable.

(l) "Methylenedianiline" or "MDA" means the chemical, 4,4'-diaminodiphenylmethane, chemical abstract service registry number 101-77-9, in the form

of a vapor, liquid, or solid. This definition also includes the salts of MDA.

(m) "Regulated areas" means areas in a workplace where airborne concentrations of MDA exceed, or can reasonably be expected to exceed, the permissible exposure limits or where dermal exposure to MDA can occur.

(n) "STEL" means short-term exposure limit as determined by a 15-minute sample period.

R 325.50053 Permissible exposure limits (PEL).

Rule 3. An employer shall ensure that an employee is not exposed to an airborne concentration of MDA that is more than 10 parts per billion (ppb) as an 8-hour, timeweighted average (TWA) or a STEL of 100 ppb.

R 325.50054 Emergency conditions; written plan; alerts.

Rule 4. (1) An employer shall develop a written plan to effectively handle emergency situations for each workplace where there is a possibility of an emergency. The plan for a construction site shall identify emergency escape routes for employees and be in place before construction operations begin. An employer shall implement appropriate portions of the plan in the event of an emergency. The emergency plan shall provide for all of the following:

(a) Plans and procedures to equip employees who are engaged in correcting emergency conditions with the appropriate personal protective equipment and clothing as required in R 325.50060 and R 325.50061 until the emergency is abated.

(b) Procedures for alerting and evacuating affected employees.

(c) Procedures for fire protection and prevention as required in R 408.41842 or R 408.10623, as applicable.

(2) If there is a possibility of employee exposure to MDA due to an emergency, then an employer shall develop means to promptly alert employees of the possibility of direct exposure. If an emergency occurs, an employer shall immediately evacuate affected employees who are not engaged in correcting emergency conditions. An employer shall develop and implement means for alerting other employees who may be exposed as a result of the emergency.

R 325.50055 Exposure monitoring generally.

Rule 5. (1) Determinations of employee exposure shall be made from breathing zone air samples that are representative of each employee's exposure to airborne MDA over an 8-hour period. Determinations of employee exposure to the STEL shall be made from breathing zone air samples collected over a 15-minute sampling period.

(2) Representative employee exposure shall be determined on the basis of 1 or more samples that represent full-shift exposure for each shift, for each job classification, and in each work area where exposure

to MDA may occur. If an employer can document that exposure levels are equivalent for similar operations in different work shifts, the employer shall only be required to determine representative employee exposure for that operation during 1 shift.

(3) Monitoring shall be accurate, to a 95% confidence level, to within plus or minus 25% of true value for airborne concentrations of MDA.

R 325.50056 Monitoring, initial, periodic, termination, and notification.

Rule 6. (1) Each employer who has a workplace or work operation that is subject to these rules shall perform initial monitoring to accurately determine an employee's exposure to airborne concentrations of MDA. Construction employers are not required to perform this initial monitoring if either of the following provisions applies:

(a) An employer can demonstrate, using objective data, that the MDA-containing product or material being handled cannot cause exposure above the action level even under a worst case release condition.

(b) An employer has historical monitoring data or other data which demonstrate that exposures on a particular job will be below the action level.

(2) If the monitoring required by the provisions of subrule (1) of this rule shows an employee's exposure to be at or above the action level, but at or below the PELs, an employer shall repeat the representative monitoring for the employee at least once every 6 months.

(3) If the monitoring required by the provisions of subrule (1) of this rule shows an employee's exposure to be above the PELs, an employer shall repeat the representative monitoring for the employee at least once every 3 months.

(4) A construction employer who conducts MDA operations within a regulated area may forgo periodic monitoring if all employees wear supplied-air respirators while working in the regulated area.

(5) An employer may alter the monitoring schedule from once every 3 months to once every 6 months for any employee for whom 2 consecutive measurements, taken not less than 7 days apart, indicate that the employee exposure has decreased to or below the TWA PEL, but at or above the action level.

(6) An employer shall perform the exposure monitoring required by the provisions of subrules (1) to (5) of this rule when there has been a change in the production process, chemicals present, control equipment, personnel, or work practices that may result in new or additional exposures to MDA or when the employer has any reason to suspect a change that may result in new or additional exposures.

(7) Both of the following provisions apply to the termination of monitoring:

(a) If the initial monitoring required by the provisions of subrule (1) of this rule shows that an employee's exposure is below the action level, the employer may discontinue the monitoring for that

employee, except as otherwise required by the provisions of subrule (6) of this rule.

(b) If the periodic monitoring required by the provisions of subrules (2) and (3) of this rule shows that an employee's exposures, as indicated by not less than 2 consecutive measurements taken not less than 7 days apart, are below the action level, the employer may discontinue the monitoring for that employee, except as otherwise required by the provisions of subrule (6) of this rule.

(8) An employer shall, within 15 working days after the receipt of the results of any monitoring performed pursuant to these rules, notify each affected employee of the monitoring results, in writing, either individually or by posting the results in an appropriate location that is accessible to affected employees. Where the PEL is exceeded, the written notification shall set forth the corrective action being taken by the employer, or identify other protective measures that have been implemented, to reduce the employee exposure to or below the PEL.

R 325.50057 Monitoring for dermal effects.

Rule 7. An employer shall make routine inspections of employee hands, faces and forearms that may have been exposed to MDA. Other potential dermal exposures that are reported by the employee shall be referred to the appropriate medical personnel for observation. If an employer determines that an employee has been exposed to MDA, the employer shall do all of the following:

(a) Determine the source of exposure.

(b) Implement protective measures to correct the hazard.

(c) Maintain records of the corrective actions in accordance with the provisions of R 325.50072.

R 325.50058 Regulated areas.

Rule 8. (1) An employer shall establish a regulated area where either of the following conditions exists:

(a) Airborne concentrations of MDA exceed, or can reasonably be expected to exceed, the permissible exposure limits.

(b) Employees are subject to dermal exposure to MDA.

(2) Regulated areas shall be demarcated from the rest of the workplace in a manner that minimizes the number of persons that might be exposed.

(3) Access to regulated areas shall be limited to authorized persons.

(4) Each person who enters a regulated area shall be supplied with, and required to use, the appropriate personal protective clothing and equipment in accordance with the provisions of R 325.50060 and R 325.50061.

(5) An employer shall ensure that employees do not eat, drink, smoke, chew tobacco or gum, or apply cosmetics in a regulated area.

R 325.50059 Methods of compliance; engineering controls; work practices; compliance program.

Rule 9. (1) An employer shall institute engineering controls and work practices to reduce and maintain employee exposure to MDA at or below the permissible exposure limits, except to the extent that the employer can establish that these controls are not feasible or if the provisions of subrule (2) of this rule or R 325.50060(1)(a) to (d) apply. Any combination of the following control methods shall be used:

(a) Local exhaust ventilation that is equipped with a high-efficiency particulate air (HEPA) filter dust collection system.

(b) A general ventilation system.

(c) Work practices.

(d) Other engineering controls, such as isolation or enclosures that the director can demonstrate to be feasible and practical.

(2) If the feasible engineering controls and work practices that can be instituted are not sufficient to reduce employee exposure to or below the PELs, an employer shall use the controls and practices to reduce employee exposure to the lowest levels achievable by the controls and practices and shall supplement them by the use of respiratory protection devices that are in compliance with the requirements of R 325.50060.

(3) A construction industry employer shall comply with both of the following provisions:

(a) Both respiratory protection and feasible engineering and work practice controls shall be used to reduce worker exposure to or below the PEL when workers are engaged in the spray application of MDA materials.

(b) Compressed air shall not be used to remove MDA material unless it is used in conjunction with an enclosed ventilation system that is designed to capture the dust cloud.

(4) An employer shall establish and implement a written compliance program to reduce employee exposure to or below the PELs by means of engineering and work practice controls, as required by subrules (1) and (2) of this rule, and through the use of respiratory protection where permitted by these rules. The program shall include a schedule for periodic maintenance, such as leak detection, and shall include a written plan for emergency situations as specified in the provisions of R 325.50054. Upon request, the written program shall be furnished, for examination and copying, to the director, affected employees, and designated employee representatives. An employer shall review and, as necessary, update the written program at least once every 12 months to make certain the program reflects the current status of compliance activities.

(5) An employer shall not use employee rotation as a means of complying with the PELs specified in R 325.50053.

R 325.50060 Respiratory protection; selection; program.

Rule 10. (1) For employees who use respirators required by these rules, an employer shall provide respirators that comply with the requirements of these rules. An employer shall ensure that employees use respirators during all of the following:

(a) Periods necessary to install or implement feasible engineering and work practice controls.

(b) Work operations for which an employer establishes that engineering and work practice controls are not feasible.

(c) Work operations for which feasible engineering and work practice controls are not yet sufficient to reduce exposure to or below the PEL.

(d) Emergencies.

(2) An employer shall select, and ensure that employees use, the appropriate respirator from table 1 of this rule. An employer shall give an employee who cannot use a negative-pressure respirator the option of using either a positive-pressure respirator or a supplied air respirator that is operated in the continuous-flow or pressure-demand mode.

(3) Table 1 reads as follows:

Table 1
Respiratory Protection for MDA

Airborne Concentrations of MDA or Condition of Use	Respirator Type
(a) Less than or equal to 10 x PEL.	Half-mask respirator with HEPA* cartridge.**
(b) Less than or equal to 50 x PEL.	Full facepiece respirator with HEPA* cartridge or canister.**
(c) Less than or equal to 1,000 x PEL.	Full facepiece, powered air-purifying respirator with HEPA* cartridges.**
(d) Greater than 1,000 x PEL or unknown concentrations.	Self-contained breathing apparatus with full facepiece in positive-pressure mode. Full facepiece, positive pressure demand supplied-air respirator with auxiliary self-contained air supply.
(e) Escape.	Any full facepiece air-purifying respirator with HEPA* cartridges.** Any positive-pressure or continuous-flow self-contained breathing apparatus with full facepiece or hood.
(f) Firefighting.	Full facepiece self-contained breathing apparatus in positive-pressure-demand mode.

Note: Respirators that are assigned for higher environmental concentrations may be used at lower concentrations.

*High-efficiency particulate air filter (HEPA) means a filter that is not less than 99.97% efficient against monodispersed particulates of 0.3 micrometers or larger.

**Combination HEPA and organic vapor cartridges shall be used if MDA is used in liquid form or in a process that requires heat.

(4) An employer shall implement a respiratory protection program in accordance with 29 C.F.R. §1910.134(b) to (d) and (f) to (m), except for (d)(1)(iii), as adopted by reference in R 325.60051 et seq. of the Michigan Administrative Code.

R 325.50061 Protective work clothing and equipment use, removal, storage, cleaning, and replacement.

Rule 11. (1) An employer shall provide, at no cost to the employee, and ensure that the employee uses, appropriate protective work clothing and equipment, such as any of the following:

- (a) Aprons, coveralls, or other full-body work clothing.
- (b) Gloves, head covers, and foot covers.
- (c) Face shields and chemical goggles.
- (d) Other appropriate protective equipment that is in compliance with the provisions of R 408.13301 et seq.

(2) The appropriate protective work clothing and equipment listed in subrule (1) of this rule shall be provided if any of the following conditions are present:

(a) The airborne concentration of MDA exceeds the PELs.

(b) An employee is subject to dermal exposure to MDA.

(c) Liquids that contain MDA can be splashed or sprayed into an employee's eyes.

(3) All of the following provisions pertain to the removal and storage of protective work clothing and equipment:

(a) At the end of an employee's work shift, an employer shall ensure that the employee removes MDA-contaminated protective work clothing and equipment, which is not routinely removed throughout the day, in change rooms that are provided in accordance with the provisions of R 325.50062.

(b) An employer shall ensure that an employee, during his or her workshift, removes all other MDA-contaminated protective work clothing or equipment before leaving a regulated area.

(c) An employer shall ensure that an employee does not take MDA-contaminated work clothing or equipment out of the change room, except for an employee who is authorized to do so for the purpose of laundering, maintenance, or disposal.

(d) MDA-contaminated work clothing or equipment shall be placed and stored in closed containers that prevent the dispersion of MDA outside the container.

(e) Containers of MDA-contaminated protective work clothing or equipment that are to be taken out of change rooms or the workplace for cleaning, maintenance, or disposal shall bear labels that warn of the hazards of MDA.

(4) All of the following provisions pertain to cleaning and replacing protective work clothing and equipment:

(a) An employer shall provide employees with clean protective work clothing and equipment. An

employer shall ensure that protective work clothing or equipment that is required by this rule is cleaned, laundered, repaired, or replaced at intervals appropriate to maintain its effectiveness.

(b) An employer shall prohibit the removal of MDA from protective work clothing or equipment by blowing, shaking, or any method that allows MDA to reenter the workplace.

(c) An employer shall ensure that laundering of MDA-contaminated clothing shall be done in a manner that prevents the release of MDA in the workplace.

(d) An employer who gives MDA-contaminated clothing to another person for laundering shall inform the person of the requirements that will prevent the release of MDA.

(e) An employer shall inform any person who launders or cleans protective clothing or equipment that is contaminated with MDA of the potentially harmful effects of exposure to MDA.

(f) MDA-contaminated clothing shall be transported in properly labeled, sealed, impermeable bags or containers.

R 325.50062 Hygiene facilities and practices for general industry.

Rule 12. (1) This rule establishes hygiene facilities and practice requirements that are applicable to all general industry employers. Construction industry employers shall comply with the provisions of R 325.50063 rather than the provisions of this rule.

(2) An employer shall provide clean change rooms for employees who must wear protective clothing or who must use protective equipment because of their exposure to MDA. Change rooms shall be equipped with separate storage for protective clothing and equipment and for street clothes and the separate storage shall prevent MDA contamination of street clothes.

(3) An employer shall ensure that employees shower at the end of a workshift if the employees work in areas where there is the potential for exposure above the action level that results from airborne MDA particulates or vapors.

All of the following provisions pertain to showers and hygiene practices:

(a) Shower facilities that are required by this subrule shall be in compliance with the provisions of occupational health rule 4201(4)(c).

(b) An employer shall ensure that employees who are required to shower pursuant to the provisions of this subrule do not leave the workplace wearing any protective clothing or equipment worn during the workshift.

(c) Where dermal exposure to MDA occurs, an employer shall ensure that materials that are spilled or deposited on the skin are removed as soon as possible by methods that do not facilitate the dermal absorption of MDA.

(4) All of the following provisions pertain to lunch facilities:

(a) If food or beverages are consumed at the worksite and employees are exposed to MDA at or above the PEL or are subject to dermal exposure to MDA, an employer shall provide a readily accessible lunch area.

(b) Lunch areas which are located within the workplace and in which there is the potential for airborne exposure to MDA at or above the PEL shall have a positive-pressure, temperature-controlled, filtered air supply.

(c) Lunch areas shall not be located in areas within the workplace where the potential for dermal exposure to MDA exists.

(d) An employer shall ensure that employees who have been subjected to dermal exposure to MDA or who have been exposed to MDA above the PEL wash their hands and faces with soap and water before eating, drinking, smoking, or applying cosmetics.

(e) An employer shall ensure that employees who are exposed to MDA do not enter lunch facilities with MDA-contaminated protective work clothing or equipment.

R 325.50063 Hygiene facilities and practices for construction industry.

Rule 13. (1) This rule applies to the construction industry only. General industry employers shall comply with the provisions of R 325.50062.

(2) An employer shall comply with either of the following provisions:

(a) An employer shall provide decontamination areas for employees who are required to work in regulated areas or who are required to wear protective clothing pursuant to the provisions of R 325.50061(1).

(b) An employer may allow employees who are working in a small-scale, short-duration operation to clean or dispose of their protective clothing before leaving the area where the work was performed.

(3) An employer shall ensure that change areas are equipped with separate storage facilities for protective clothing and street clothing in accordance with the provisions of occupational health rule 4201(5).

(4) An equipment area shall be supplied with impermeable, labeled bags and containers for the containment and disposal of contaminated protective clothing and equipment.

(5) Both of the following provisions apply to employee hygiene:

(a) Where feasible, shower facilities shall be provided that are in compliance with the provisions of occupational health rule 4201(4)(c) if the possibility of employee exposure to airborne levels of MDA in excess of the permissible exposure limit exists.

(b) Where dermal exposure to MDA occurs, an employer shall ensure that materials that are spilled or deposited on the skin are removed as soon as possible by methods that do not facilitate the dermal absorption of MDA.

(6) All of the following provisions apply to lunch facilities:

(a) If food or beverages are consumed at the worksite and if employees are exposed to MDA, an employer shall provide a clean lunch area where MDA levels are below the action level and where dermal exposure to MDA cannot occur.

(b) An employer shall ensure that employees wash their hands and faces with soap and water before eating, drinking, smoking, or applying cosmetics.

(c) An employer shall ensure that employees do not enter lunch facilities with contaminated protective work clothing or equipment.

R 325.50064 Communication of hazards to employees.

Rule 14. (1) Both of the following provisions pertain to signs and labels:

(a) An employer shall post and maintain legible signs that demarcate regulated areas and entrances or accessways to regulated areas that bear the following legend:

**DANGER
MDA
MAY CAUSE CANCER
LIVER TOXIN
AUTHORIZED PERSONNEL ONLY
RESPIRATORS AND PROTECTIVE CLOTHING
MAY BE REQUIRED TO BE WORN IN THIS AREA**

(b) An employer shall ensure that labels or other appropriate forms of warning are provided for containers of MDA within the workplace. The labels shall be in compliance with the requirements of paragraph (f) of the occupational safety and health administration (OSHA) hazard communication standard, being 29 C.F.R. §1910.1200(f), which is incorporated by section 14a of Act No. 154 of the Public Acts of 1974, as amended, being §408.1014a of the Michigan Compiled Laws, and shall include either of the following legends:

(i) For pure MDA

**DANGER
CONTAINS MDA
MAY CAUSE CANCER
LIVER TOXIN**

(ii) For mixtures containing MDA

**DANGER
CONTAINS MDA
CONTAINS MATERIALS WHICH MAY CAUSE
CANCER
LIVER TOXIN**

(2) Both of the following provisions pertain to material safety data sheets (MSDS):

(a) An employer shall obtain or develop, and shall provide employees access to a material safety data

sheet (MSDS) for MDA. In meeting this obligation, an employer shall make appropriate use of the information provided in appendices A and B to these rules.

(b) An employer who is a manufacturer or importer of MDA shall comply with both of the following provisions:

(i) Comply with the provisions of subrule (1) of this rule, as appropriate.

(ii) Comply with the provisions of paragraph (g) of the hazard communication standard, 29 C.F.R. §1910.1200, which require the furnishing of an MSDS to downstream employers who use MDA.

(3) All of the following provisions pertain to employee information and training:

(a) An employer shall provide employees with information and training on MDA in accordance with the provisions of paragraph (h) of the hazard communication standard at the time of their initial assignment of work that will involve exposure to MDA and at least annually thereafter.

(b) An employer shall inform employees of all of the following:

(i) An explanation of the contents of these rules, including appendices A and B, and inform employees where a copy of these rules is available for inspection.

(ii) The medical surveillance program that is required by the provision of R 325.50066 to R 325.50069 and an explanation of the information contained in appendix C.

(iii) The medical removal provision required by the provisions of R 325.50070 and R 325.50071.

(c) An employer shall make all written materials that relate to the employee training program, including a copy of these rules and appendices, readily available to all affected employees, without cost.

(d) An employer shall provide to the director, upon request, all of the information and training materials that relate to the employee information and training program required by the provisions of this subrule.

R 325.50065 Housekeeping.

Rule 15. All of the following provisions pertain to housekeeping:

(a) All surfaces shall be maintained as free as practical of the visible accumulation of MDA.

(b) An employer shall institute a program for detecting MDA leaks, spills, and discharges, including regular visual inspection of operations in which liquid or solid MDA is used.

(c) All leaks shall be repaired and liquid or dust spills cleaned up promptly.

(d) Surfaces that are contaminated with MDA shall not be cleaned using compressed air.

(e) Shovel, dry sweeping, and other methods of dry clean-up of MDA may be used only where HEPA-filtered vacuuming and wet cleaning are not feasible or practical.

(f) Waste, scrap, debris, bags, containers, equipment, and clothing contaminated with MDA shall

be collected and disposed of in a manner to prevent the reentry of MDA into the workplace.

R 325.50066 Medical surveillance generally.

Rule 16. (1) An employer shall establish and make available a medical surveillance program for all of the following:

(a) Employees who are exposed at or above the action level for 30 or more days per year.

(b) Employees who are subject to dermal exposure to MDA for 15 or more days per year.

(c) Employees who have been exposed to MDA in an emergency situation.

(d) Employees whom the employer, based on results from compliance with the provisions of R 325.50057, has reason to believe are being dermally exposed.

(e) Employees who show signs or symptoms of MDA exposure.

(2) An employer shall ensure that all medical examinations and procedures are performed by, or under the supervision of, a licensed physician, at a reasonable time and place, and provided without cost to the employee.

R 325.50067 Medical examinations; initial, periodic, emergency, and additional.

Rule 17. (1) Within 150 days of the effective date of these rules, or before the time of initial assignment, an employer shall provide each employee who is specified by the provisions of R 325.50066(1) with an initial medical examination that includes all of the following elements:

(a) A detailed history that includes all of the following information:

(i) Past work exposure to MDA or any other toxic substances.

(ii) A history of drugs, alcohol, tobacco, and medications that are routinely taken, including the duration and quantity.

(iii) A history of dermatitis, chemical skin sensitization, or previous hepatic disease.

(b) A physical examination that includes all normal components of a routine physical examination and an examination of the skin and an examination for signs of liver disease.

(c) Laboratory tests, including liver function tests and urinalysis.

(d) Additional tests as necessary in the opinion of the physician.

(2) An initial medical examination is not required if adequate records show that an employee has been examined in accordance with the requirements of subrule (1) of this rule before the date of initial assignment or within the 6-month period before the effective date of these rules.

(3) An employer shall provide each employee who is specified in the provisions of R 325.50066(1) with a periodic medical examination at least annually

following the initial examination. A periodic examination shall include all of the following elements:

(a) A brief history of any new exposure to potential liver toxins; changes in drug, tobacco, or alcohol intake; and the appearance of physical signs that relate to the liver and the skin.

(b) The appropriate tests and examinations, including liver function tests and skin examinations.

(c) Appropriate additional tests or examinations as deemed necessary by the physician.

(4) If, in the physician's opinion, the results of liver function tests indicate an abnormality, an employee shall be removed from further MDA exposure in accordance with the provisions of R 325.50070. Repeat liver function tests shall be conducted as recommended by the physician.

(5) If an employer determines that an employee has been exposed to a potentially hazardous amount of MDA in an emergency situation as addressed by the provisions of R 325.50054, the employer shall provide medical examinations in accordance with the provisions of subrules (3) and (4) of this rule. If the results of liver function testing indicate an abnormality, the employee shall be removed in accordance with the provisions of R 325.50070. Repeat liver function tests shall be conducted on the advice of the physician. If the results of the tests are normal, tests shall be repeated 2 to 3 weeks from the initial testing. If the results of the second set of tests are normal and if on the advice of the physician, additional testing is not required.

(6) If an employee develops signs and symptoms that are associated with exposure to MDA, an employer shall provide the employee with an additional medical examination, including a liver function test. Repeat liver function tests shall be conducted on the advice of the physician. If the results of the tests are normal, tests shall be repeated 2 to 3 weeks from the initial testing. If the results of the second set of tests are normal and if on the advice of the physician, additional testing is not required.

R 325.50068 Multiple physician review.

Rule 18. (1) If an employer selects the initial physician who conducts any medical examination or consultation provided to an employee pursuant to these rules, if the employee has signs or symptoms of occupational exposure to MDA, which could include an abnormal liver function test, if the employee disagrees with the opinion of the examining physician, and if the opinion could affect the employee's job status, then the employee may designate an appropriate, mutually acceptable second physician to do both of the following:

(a) Review any findings, determinations, or recommendations of the initial physician.

(b) Conduct such examinations, consultations, and laboratory tests as the second physician deems necessary to facilitate the review.

(2) An employer shall promptly notify an employee of the right to seek a second medical opinion after each occasion that an initial physician conducts a medical examination or consultation pursuant to the provisions of these rules. The employer may condition its participation in, and payment for, the multiple physician review mechanism upon the employee doing both of the following within 15 days after receipt of the foregoing notification or receipt of the initial physician's written opinion, whichever is later:

(a) Informing the employer that he or she intends to seek a second medical opinion.

(b) Initiating steps to make an appointment with a second physician.

(3) If the findings, determinations, or recommendations of the second physician differ from those of the initial physician, then the employer and the employee shall ensure that efforts are made for the 2 physicians to resolve any disagreement.

(4) If the 2 physicians have been unable to quickly resolve their disagreement, then the employer and the employee, through their respective physicians, shall designate a third physician to do both of the following:

(a) Review any findings, determinations, or recommendations of the previous physicians.

(b) Conduct such examinations, consultations, laboratory tests, and discussions with the previous physicians as the third physician deems necessary to resolve the disagreement of the previous physicians.

(5) An employer shall act consistent with the findings, determinations, and recommendations of the third physician, unless the employer and the employee reach an agreement that is otherwise consistent with the recommendations of at least 1 of the 3 physicians.

R 325.50069 Information provided to a physician; physician's opinion.

Rule 19. (1) An employer shall provide all of the following information to the examining physician:

(a) A copy of these rules and appendices.

(b) A description of the affected employee's duties as they relate to the employee's potential exposure to MDA.

(c) The employee's current actual or representative MDA exposure level.

(d) A description of any personal protective equipment that is used or to be used.

(e) Information from previous employment-related medical examinations of the affected employee.

(2) An employer shall provide the information required by the provisions of subrule (1) of this rule to a second physician upon a request either by the second physician or by the employee.

(3) For each medical examination that is conducted pursuant to the provisions of these rules, an employer shall obtain, and provide the employee with a copy of, the examining physician's written opinion within 15 days of receipt of the opinion. The written opinion shall include all of the following:

(a) The occupationally pertinent results of the medical examination and tests.

(b) The physician's opinion concerning whether the employee has any detected medical conditions that would place the employee at increased risk of material impairment of health from exposure to MDA.

(c) The physician's recommended limitations upon the employee's exposure to MDA or upon the employee's use of protective clothing or equipment and respirators.

(d) A statement that the employee has been informed by the physician of the results of the medical examination and any medical conditions resulting from MDA exposure that require further explanation or treatment.

(4) The written opinion obtained by the employer shall not reveal specific findings or diagnoses unrelated to occupational exposures.

R 325.50070 Medical removal; return to job.

Rule 20. (1) After any medical examination specified by the provisions of R 325.50067, an employee shall be removed from work environments in which exposure to MDA is at or above the action level or where dermal exposure to MDA may occur in either of the following situations:

(a) When the employee exhibits signs or symptoms, or both, indicative of acute exposure to MDA.

(b) When the examining physician determines that an employee's abnormal liver function tests are not associated with MDA exposure, but that the abnormalities may be exacerbated as a result of occupational exposure to MDA.

(2) An employer shall remove an employee from work environments in which exposure to MDA is at or above the action level or where dermal exposure to MDA may occur if there is a final medical determination or opinion that the employee has a detected medical condition that places the employee at increased risk of material impairment to health from exposure to MDA.

(3) For the purposes of this rule, the phrase "final medical determination" means the outcome of the physician review mechanism that is used pursuant to the medical surveillance provisions of these rules.

(4) Where a final medical determination results in any recommended special protective measures for an employee or a limitation on an employee's exposure to MDA, the employer shall implement, and act consistent with, the recommendation.

(5) An employer shall return an employee to his or her former job status in either of the following situations:

(a) Upon the advice of the physician or when the employee no longer shows signs or symptoms of exposure to MDA.

(b) When a subsequent final medical determination results in a medical finding, determination, or opinion that the employee no longer

has a detected medical condition that places the employee at increased risk of material impairment to health from exposure to MDA.

(6) For the purposes of these rules, the requirement that an employer return an employee to his or her former job status is not intended to expand upon or restrict any rights an employee has or would have had, absent temporary medical removal, to a specific job classification or position under the terms of a collective bargaining agreement.

(7) An employer shall remove any limitations placed on an employee, or end any special protective measures provided to an employee, pursuant to a final medical determination when a subsequent final medical determination indicates that the limitations or special protective measures are no longer necessary.

(8) Where the physician review mechanism that is used pursuant to the medical surveillance provisions of these rules has not yet resulted in a final medical determination with respect to an employee, an employer shall act as follows:

(a) The employer may remove the employee from exposure to MDA, provide special protective measures to the employee, or place limitations upon the employee consistent with the medical findings, determinations, or recommendations of any of the physicians who have reviewed the employee's health status.

(b) The employer may return the employee to his or her former job status and end any special protective measures provided to the employee consistent with the medical findings, determinations, or recommendations of any of the physicians who have reviewed the employee's health status, with the 2 following exceptions:

(i) If the initial removal, special protection, or limitation of the employee resulted from a final medical determination that differed from the findings, determinations, or recommendations of the initial physician.

(ii) If the employee has been on removal status for the preceding 6 months as a result of exposure to MDA, then the employer shall await a final medical determination.

R 325.50071 Medical removal protection benefits.

Rule 21. (1) An employer shall provide to an employee up to 6 months of medical removal protection benefits on each occasion that an employee is removed from exposure to MDA or is otherwise limited pursuant to these rules.

(2) For the purposes of this rule, the requirement that an employer provide medical removal protection benefits means that the employer shall maintain the earnings, seniority, and other employment rights and benefits of an employee as though the employee had not been removed from normal exposure to MDA or otherwise limited.

(3) During the period of time that an employee is removed from normal exposure to MDA or otherwise

limited, the employer may condition the provision of medical removal protection benefits upon the employee's participation in follow-up medical surveillance made available pursuant to these rules.

(4) If a removed employee files a claim for workers' compensation payments for a MDA-related disability, then an employer shall continue to provide medical removal protection benefits pending disposition of the claim. To the extent that an award is made to the employee for earnings lost during the period of removal, the employer's medical removal protection obligation shall be reduced by such amount. The employer shall receive no credit for workers' compensation payments received by the employee for treatment-related expenses.

(5) An employer's obligation to provide medical removal protection benefits to a removed employee shall be reduced to the extent that the employee receives compensation for earnings lost during the period of removal either from a publicly funded or employer-funded compensation program or receives income from non-MDA-related employment with any employer that is made possible by virtue of the employee's removal.

(6) An employer shall take all of the following measures with respect to any employee who is medically removed from exposure to MDA:

(a) The employer shall make available to the employee a medical examination pursuant to the provisions of these rules to obtain a final medical determination with respect to the employee.

(b) The employer shall assure that the final medical determination obtained indicates whether or not the employee may be returned to his or her former job status. If return is not recommended, the final medical determination shall specify what measures should be taken to protect the employee's health.

(c) If the final medical determination has not yet been obtained or, once obtained, indicates that the employee may not yet be returned to his or her former job status, the employer shall continue to provide medical removal protection benefits to the employee until either the employee is returned to former job status or a final medical determination is made that the employee is incapable of ever safely returning to his or her former job status.

(d) If the employer acts pursuant to a final medical determination that permits the return of the employee to his or her former job status despite what would otherwise be an abnormal liver function test, later questions concerning removing the employee again shall be decided pursuant to a final medical determination. The employer need not automatically remove such an employee pursuant to the MDA removal criteria provided by these rules.

(7) If an employer, although not required by these rules to do so, removes an employee from exposure to MDA or otherwise places limitations on an employee due to the effects of MDA exposure on the employee's medical condition, the employer shall provide medical

removal protection benefits to the employee equal to that required by the provisions of subrules (1) and (2) of this rule.

R 325.50072 Recordkeeping.

Rule 22. (1) This subrule applies to general industry employers only. If, as a result of the initial monitoring, the processing, use, or handling of products that are made from or contain MDA is exempted from other requirements of these rules pursuant to the provisions of R 325.50051(2), an employer shall establish and maintain an accurate record of the monitoring relied on in support of the exemption.

(2) This subrule applies only to construction industry employers. If an employer has relied on objective data that demonstrate that products made from or containing MDA are not capable of releasing MDA or do not present a dermal exposure problem under the expected conditions of processing, use, or handling to exempt such operations from the initial monitoring requirements of R 325.50056(1), then the employer shall establish and maintain an accurate record of the objective data that was reasonably relied upon in support of the exemption.

(3) The record required pursuant to the provisions of subrule (1) or (2) of this rule shall be maintained for the duration of the employer's reliance on the record and shall include all of the following information:

(a) The product that qualifies for exemption.

(b) The source of the monitoring data; was monitoring performed by the employer or a private contractor.

(c) The testing protocol, results of testing, and analysis of the material for the release of MDA.

(d) A description of the operation that was exempted and an explanation of how the data support the exemption.

(e) Other data that are relevant to the operations, materials, processing, or employee exposures covered by the exemption.

(4) This subrule applies to general industry employees only. If the processing, use, or handling of products made from or containing MDA are exempted from other requirements of these rules as provided in R 325.50051, the employer shall establish and maintain an accurate record of objective data that were relied upon in support of the exemption. The record shall be maintained for the duration of the employer's reliance upon the data. The record shall include all of the following information:

(a) The product that qualifies for exemption.

(b) The source of the objective data.

(c) The testing protocol.

(d) The results of testing and analysis of the material for the release of MDA.

(e) A description of the operation that was exempted and an explanation of how the data supports the exemption.

(f) Other data that are relevant to the operations, materials, processing, or employee exposures covered by the exemption.

(5) This subrule applies to construction industry employers only. If an employer has relied on historical monitoring data to demonstrate that exposures on a particular job will be below the action level and exempt such operations from the initial monitoring required by the provisions of R 325.50056(1), then the employer shall establish and maintain an accurate record of the historical monitoring data that were reasonably relied upon in support of the exemption. The record shall be maintained for the duration of the employer's reliance upon the data. The record shall include all of the following information:

(a) Documentation that the data upon which judgments are based are scientifically sound and were collected using methods that are sufficiently accurate and precise.

(b) Evidence that the processes and work practices that were in use when the data were obtained are essentially the same as those to be used for the job for which initial monitoring will not be performed.

(c) Evidence that the characteristics of the MDA-containing material being used when the historical data were obtained are the same as those on the job for which initial monitoring will not be performed.

(d) Evidence that the environmental conditions prevailing when the historical monitoring data were obtained are the same as those on the job for which initial monitoring will not be performed.

(e) Other data that are relevant to the operations, materials, processing, or employee exposures covered by the exemption. An employer may use the services of a competent organization, such as an industry trade association and an employee association, to maintain the records required by these rules.

(6) An employer shall establish and maintain an accurate record of all exposure monitoring measurements required by the provisions of R 325.50055 to R 325.50057. The records shall be maintained for not less than 30 years and access to the records shall be provided in accordance with the provisions of R 325.3451 et seq. The record shall include all of the following information:

(a) The dates, number, duration, and results of each of the samples taken.

(b) A description of the procedure that was used to determine representative employee exposures.

(c) Identification of the sampling and analytical methods that were used.

(d) A description of the type of respiratory and other protective devices that were worn, if any.

(e) The name, social security number, job classification, and exposure levels of the employees whose exposures are represented.

(7) An employer shall establish and maintain, in accordance with the provisions of R 325.3451 et seq., accurate medical surveillance records for each

employee who is subject to the medical surveillance required by the provisions of R 325.50066 to R 325.50070. The records shall include all of the following information:

(a) The name, social security number, and description of the duties of an employee.

(b) The employer's copy of the physician's written opinion on the initial, periodic, and any special examinations, including the results of the medical examination and all tests, opinions, and recommendations.

(c) The results of any airborne exposure monitoring that was performed for an employee and the representative exposure levels supplied to the physician.

(d) Any employee medical complaints that are related to exposure to MDA.

(e) Information that is provided to the physician as required by the provisions of R 325.50069(1).

(8) This subrule applies only to a general industry employer. An employer shall keep, or assure that the examining physician keeps, all of the following medical records:

(a) A copy of these rules and appendices, except that the employer may keep 1 copy of these rules and appendices for all employees if the employer references these rules and appendices in the medical surveillance record of each employee.

(b) A copy of the information that is provided to the physician as required by the provisions of R 325.50069(1).

(c) A description of the laboratory procedures and a copy of any standards or guidelines that were used to interpret the test results or references to the information.

(d) A copy of the employee's medical and work history that is related to exposure to MDA.

(9) This subrule applies to general industry employers only. An employer shall establish and maintain an accurate record for each employee who is removed from current exposure to MDA pursuant to the provisions of R 325.50070. The medical removal records shall be maintained for not less than the duration of the employee's employment plus 30 years. Each record shall include all of the following information:

(a) The name and social security number of the employee.

(b) The date of each occasion that the employee was removed from current exposure to MDA and the corresponding date on which the employee was returned to his or her former job status.

(c) A brief explanation of how each removal was or is being accomplished.

(d) A statement that indicates the reason for the removal.

(10) An employer shall make records available for examination and copying in accordance with the following provisions and the provisions of R 325.3451 et seq.:

(a) Any record that is required by this rule shall be available, upon request, to the director.

(b) Any employee exposure monitoring record that is required by this rule shall be provided, upon request, to the employee and a designated employee representative.

(c) Any employee medical record that is required by this rule shall be provided, upon request, to the subject employee and a designated employee representative.

(11) An employer shall comply with the requirements that involve the transfer of records in accordance with the provisions of R 325.3475. If an employer ceases to do business and there is no successor employer to receive and retain the records for the prescribed period, the employer shall notify the director not less than 90 days before disposal of the records and shall transmit the records to the director if requested by the director within that period.

R 325.50073 Observation of monitoring.

Rule 23. (1) An employer shall provide affected employees, or their designated representatives, an opportunity to observe the measuring or monitoring of employee exposure to MDA that is conducted pursuant to the provisions of R 325.50055 to R 325.50057.

(2) When observation of the measuring or monitoring of employee exposure to MDA requires entry into areas where the use of protective clothing and equipment or respirators is required, an employer shall provide the observer with personal protective clothing and equipment or respirators required to be worn by employees working in the areas, assure the use of such clothing and equipment or respirators, and require the observer to comply with all other applicable safety and health procedures.

R 325.50074 RESCINDED

R 325.50075 Appendices.

Rule 25. Appendices A, B, C, and D to these rules are informational only and are not intended to create any additional obligations or requirements not otherwise imposed by these rules or to detract from any established obligations or requirements.

R 325.50076 Availability of rules and appendices; permission to copy.

Rule 26. (1) Copies of these rules and appendices are available at no cost from the Michigan Department of Consumer and Industry Services, Standards Division, P.O. Box 30643, Lansing, Michigan 48909.

(2) Permission to copy any of these documents in full is granted by the director.

APPENDICES TO MIOSHA STANDARD FOR METHYLENEDIANILINE (MDA) (R325.50051 - R 325.50076)

APPENDIX A TO 1910.1050 AND 1926.60-- SUBSTANCE DATA SHEET FOR 4-4'- METHYLENEDIANILINE

I. SUBSTANCE IDENTIFICATION

A. Substance: Methylenedianiline (MDA)

B. Permissible Exposure:

1. Airborne: Ten parts per billion parts of air (10 ppb), time-weighted average (TWA) for an 8-hour workday and an action level of five parts per billion parts of air (5 ppb).

2. Dermal: Eye contact and skin contact with MDA are not permitted.

C. Appearance and odor: White to tan solid; amine odor.

II. HEALTH HAZARD DATA

A. Ways in which MDA affects your health. MDA can affect your health if you inhale it, or if it comes in contact with your skin or eyes. MDA is also harmful if you happen to swallow it. Do not get MDA in eyes, on skin, or on clothing.

B. Effects of overexposure. 1. Short-term (acute) overexposure: Overexposure to MDA may produce fever, chills, loss of appetite, vomiting, jaundice. Contact may irritate skin, eyes and mucous membranes. Sensitization may occur.

2. Long-term (chronic) exposure. Repeated or prolonged exposure to MDA, even at relatively low concentrations, may cause cancer. In addition, damage to the liver, kidneys, blood, and spleen may occur with long-term exposure.

3. Reporting signs and symptoms: You should inform your employer if you develop any signs or symptoms which you suspect are caused by exposure to MDA including yellow staining of the skin.

III. PROTECTIVE CLOTHING AND EQUIPMENT

A. Respirators. Respirators are required for those operations in which engineering controls or work practice controls are not adequate or feasible to reduce exposure to the permissible limit. If respirators are worn, they must have a label issued by the National Institute for Occupational Safety and Health under the provisions of 42 CFR part 84 stating that the respirators have been approved for this purpose, and cartridges and canisters must be replaced in accordance with the requirements of R 325.60051 et seq., Respiratory Protection. If you experience difficulty breathing while wearing a respirator, you may request a positive pressure respirator from your employer. You must be thoroughly trained to use the assigned respirator, and the training will be provided by your employer.

MDA does not have a detectable odor except at levels well above the permissible exposure limits. Do not depend on odor to warn you when a respirator canister is exhausted. If you can smell MDA while wearing a respirator, proceed immediately to fresh air.

If you experience difficulty breathing while wearing a respirator, tell your employer.

B. Protective Clothing. You may be required to wear coveralls, aprons, gloves, face shields, or other appropriate protective clothing to prevent skin contact with MDA. Where protective clothing is required, your employer is required to provide clean garments to you, as necessary, to assure that the clothing protects you adequately. Replace or repair impervious clothing that has developed leaks.

MDA should never be allowed to remain on the skin. Clothing and shoes which are not impervious to MDA should not be allowed to become contaminated with MDA, and if they do, the clothing and shoes should be promptly removed and decontaminated. The clothing should be laundered to remove MDA or discarded. Once MDA penetrates shoes or other leather articles, they should not be worn again.

C. Eye protection. You must wear splashproof safety goggles in areas where liquid MDA may contact your eyes. Contact lenses should not be worn in areas where eye contact with MDA can occur. In addition, you must wear a face shield if your face could be splashed with MDA liquid.

IV. Emergency and First Aid Procedures.

A. Eye and face exposure. If MDA is splashed into the eyes, wash the eyes for at least 15 minutes. See a doctor as soon as possible.

B. Skin exposure. If MDA is spilled on your clothing or skin, remove the contaminated clothing and wash the exposed skin with large amounts of soap and water immediately. Wash contaminated clothing before you wear it again.

C. Breathing. If you or any other person breathes in large amounts of MDA, get the exposed person to fresh air at once. Apply artificial respiration if breathing has stopped. Call for medical assistance or a doctor as soon as possible. Never enter any vessel or confined space where the MDA concentration might be high without proper safety equipment and at least one other person present who will stay outside. A life line should be used.

D. Swallowing. If MDA has been swallowed and the patient is conscious, do not induce vomiting. Call for medical assistance or a doctor immediately.

V. MEDICAL REQUIREMENTS

If you are exposed to MDA at a concentration at or above the action level for more than 30 days per year, or exposed to liquid mixtures more than 15 days per year, your employer is required to provide a medical examination, including a medical history and laboratory tests, within 60 days of the effective date of this standard and annually thereafter. These tests shall be provided without cost to you. In addition, if you are accidentally exposed to MDA (either by ingestion, inhalation, or skin/eye contact) under conditions known or suspected to constitute toxic exposure to MDA, your

employer is required to make special examinations and tests available to you.

VI. OBSERVATION OF MONITORING

Your employer is required to perform measurements that are representative of your exposure to MDA and you or your designated representative are entitled to observe the monitoring procedure. You are entitled to observe the steps taken in the measurement procedure and to record the results obtained. When the monitoring procedure is taking place in an area where respirators or personal protective clothing and equipment are required to be worn, you and your representative must also be provided with, and must wear, the protective clothing and equipment.

VII. ACCESS TO RECORDS

You or your representative are entitled to see the records of measurements of your exposure to MDA upon written request to your employer. Your medical examination records can be furnished to your physician or designated representative upon request by you to your employer.

VIII. PRECAUTIONS FOR SAFE USE, HANDLING AND STORAGE

A. Material is combustible. Avoid strong acids and their anhydrides. Avoid strong oxidants. Consult supervisor for disposal requirements.

B. Emergency clean up. Wear self-contained breathing apparatus and fully clothe the body in the appropriate personal protective clothing and equipment.

APPENDIX B--SUBSTANCE TECHNICAL GUIDELINES, MDA

I. IDENTIFICATION

A. Substance identification.

1. Synonyms: CAS No. 101-77-9. 4,4'-methylenedianiline; 4,4'-methylenebis(aniline); methylenedianiline; dianilinomethane.

2. Formula: $C_{13}H_{14}N_2$

II. PHYSICAL DATA

1. Appearance and Odor: White to tan solid; amine odor

2. Molecular Weight: 198.26

3. Boiling Point: 398-399 degrees C at 760 mm Hg

4. Melting Point: 88-93 degrees C (190-100 degrees F)

5. Vapor Pressure: 9 mmHg at 232 degrees C

6. Evaporation Rate (n-butyl acetate = 1): Negligible

7. Vapor Density (Air=1): Not Applicable

8. Volatile Fraction by Weight: Negligible

9. Specific Gravity (Water=1): Slight

10. Heat of Combustion: -8.40 kcal/g

11. Solubility in Water: Slightly soluble in cold water, very soluble in alcohol, benzene, ether, and many organic solvents.

III. FIRE, EXPLOSION, AND REACTIVITY HAZARD DATA

1. Flash Point: 190 degrees C (374 degrees F) Setaflash closed cup
2. Flash Point: 226 degrees C (439 degrees F) Cleveland open cup
3. Extinguishing Media: Water spray; Dry Chemical; Carbon dioxide.
4. Special Fire Fighting Procedures: Wear self-contained breathing apparatus and protective clothing to prevent contact with skin and eyes.
5. Unusual Fire and Explosion Hazards: Fire or excessive heat may cause production of hazardous decomposition products.

IV. REACTIVITY DATA

1. Stability: Stable
2. Incompatibility: Strong oxidizers
3. Hazardous Decomposition Products: As with any other organic material, combustion may produce carbon monoxide. Oxides of nitrogen may also be present.
4. Hazardous Polymerization: Will not occur.

V. SPILL AND LEAK PROCEDURES

1. Sweep material onto paper and place in fiber carton.
2. Package appropriately for safe feed to an incinerator or dissolve in compatible waste solvents prior to incineration.
3. Dispose of in an approved incinerator equipped with afterburner and scrubber or contract with licensed chemical waste disposal service.
4. Discharge treatment or disposal may be subject to federal, state, or local laws.
5. Wear appropriate personal protective equipment.

VI. SPECIAL STORAGE AND HANDLING PRECAUTIONS

- A. High exposure to MDA can occur when transferring the substance from one container to another. Such operations should be well ventilated and good work practices must be established to avoid spills.
- B. Pure MDA is a solid with a low vapor pressure. Grinding or heating operations increase the potential for exposure.
- C. Store away from oxidizing materials.
- D. Employers shall advise employees of all areas and operations where exposure to MDA could occur.

VII. HOUSEKEEPING AND HYGIENE FACILITIES

- A. The workplace should be kept clean, orderly, and in a sanitary condition. The employer should institute a leak and spill detection program for

operations involving MDA in order to detect sources of fugitive MDA emissions.

B. Adequate washing facilities with hot and cold water are to be provided and maintained in a sanitary condition. Suitable cleansing agents should also be provided to assure the effective removal of MDA from the skin.

VIII. COMMON OPERATIONS

Common operations in which exposure to MDA is likely to occur include the following: Manufacture of MDA; Manufacture of Methylene diisocyanate; Curing agent for epoxy resin structures; Wire coating operations; and filament winding.

APPENDIX C--MEDICAL SURVEILLANCE GUIDELINES FOR MDA

I. ROUTE OF ENTRY

Inhalation; skin absorption; ingestion. MDA can be inhaled, absorbed through the skin, or ingested.

II. TOXICOLOGY

MDA is a suspect carcinogen in humans. There are several reports of liver disease in humans and animals resulting from acute exposure to MDA. A well documented case of an acute cardiomyopathy secondary to exposure to MDA is on record. Numerous human cases of hepatitis secondary to MDA are known. Upon direct contact MDA may also cause damage to the eyes. Dermatitis and skin sensitization have been observed. Almost all forms of acute environmental hepatic injury in humans involve the hepatic parenchyma and produce hepatocellular jaundice. This agent produces intrahepatic cholestasis. The clinical picture consists of cholestatic jaundice, preceded or accompanied by abdominal pain, fever, and chills. Onset in about 60% of all observed cases is abrupt with severe abdominal pain. In about 30% of observed cases, the illness presented and evolved more slowly and less dramatically, with only slight abdominal pain. In about 10% of the cases only jaundice was evident. The cholestatic nature of the jaundice is evident in the prominence of itching, the histologic predominance of bile stasis, and portal inflammatory infiltration, accompanied by only slight parenchymal injury in most cases, and by the moderately elevated transaminase values. Acute, high doses, however, have been known to cause hepatocellular damage resulting in elevated SGPT, SGOT, alkaline phosphatase and bilirubin.

Absorption through the skin is rapid. MDA is metabolized and excreted over a 48-hour period. Direct contact may be irritating to the skin, causing dermatitis. Also MDA which is deposited on the skin is not thoroughly removed through washing.

MDA may cause bladder cancer in humans. Animal data supporting this assumption is not available nor is conclusive human data. However, human data collected on workers at a helicopter

manufacturing facility where MDA is used suggests a higher incidence of bladder cancer among exposed workers.

III. SIGNS AND SYMPTOMS

Skin may become yellow from contact with MDA.

Repeated or prolonged contact with MDA may result in recurring dermatitis (red-itchy, cracked skin) and eye irritation. Inhalation, ingestion or absorption through the skin at high concentrations may result in hepatitis, causing symptoms such as fever and chills, nausea and vomiting, dark urine, anorexia, rash, right upper quadrant pain and jaundice. Corneal burns may occur when MDA is splashed in the eyes.

IV. TREATMENT OF ACUTE TOXIC EFFECTS/ EMERGENCY SITUATION

If MDA gets into the eyes, immediately wash eyes with large amounts of water. If MDA is splashed on the skin, immediately wash contaminated skin with mild soap or detergent. Employee should be removed from exposure and given proper medical treatment. Medical tests required under the emergency section of the medical surveillance section (M)(4) must be conducted.

If the chemical is swallowed, do not induce vomiting but remove by gastric lavage.

APPENDIX D--SAMPLING AND ANALYTICAL METHODS FOR MDA MONITORING AND MEASUREMENT PROCEDURES

Measurements taken for the purpose of determining employee exposure to MDA are best taken so that the representative average 8-hour exposure may be determined from a single 8-hour sample or two (2) 4-hour samples. Short-time interval samples (or grab samples) may also be used to determine average exposure level if a minimum of five measurements are taken in a random manner over the 8-hour work shift. Random sampling means that any portion of the work shift has the same chance of being sampled as any other. The arithmetic average of all such random samples taken on one work shift is an estimate of an employee's average level of exposure for that work shift. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

There are a number of methods available for monitoring employee exposures to MDA. The method OSHA currently uses is included below.

The employer however has the obligation of selecting any monitoring method which meets the accuracy and precision requirements of the standard under his unique field conditions. The standard requires that the method of monitoring must have an accuracy, to a 95 percent confidence level, of not less than plus or minus 25 percent for the select PEL.

OSHA METHODOLOGY

Sampling Procedure

Apparatus

Samples are collected by use of a personal sampling pump that can be calibrated within + 5% of the recommended flow rate with the sampling filter in line.

Samples are collected on 37 mm Gelman type A/E glass fiber filters treated with sulfuric acid. The filters are prepared by soaking each filter with 0.5 mL of 0.26N H₂SO₄. (0.26 N H₂SO₄ can be prepared by diluting 1.5 mL of 36N H₂SO₄ to 200 mL with deionized water.) The filters are dried in an oven at 100 degrees C for one hour and then assembled into two-piece 37 mm polystyrene cassettes with backup pads. The cassettes are sealed with shrink bands and the ends are plugged with plastic plugs.

After sampling, the filters are carefully removed from the cassettes and individually transferred to small vials containing approximately 2 mL deionized water. The vials must be tightly sealed. The water can be added before or after the filters are transferred. The vials must be sealable and capable of holding at least 7 mL of liquid. Small glass scintillation vials with caps containing Teflon liners are recommended.

Reagents

Deionized water is needed for addition to the vials.

Sampling technique

Immediately before sampling, remove the plastic plugs from the filter cassettes.

Attach the cassette to the sampling pump with flexible tubing and place the cassette in the employee's breathing zone.

After sampling, seal the cassettes with plastic plugs until the filters are transferred to the vials containing deionized water.

At some convenient time within 10 hours of sampling, transfer the sample filters to vials.

Seal the small vials lengthwise.

Submit at least one blank filter with each sample set. Blanks should be handled in the same manner as samples, but no air is drawn through them.

Record sample volumes (in L of air) for each sample, along with any potential interferences.

Retention efficiency

A retention efficiency study was performed by drawing 100 L of air (80% relative humidity) at 1 L/min through sample filters that had been spiked with 0.814 ug MDA. Instead of using backup pads, blank acid-treated filters were used as backups in each cassette.

Upon analysis, the top filters were found to have an average of 91.8% of the spiked amount. There was no MDA found on the bottom filters, so the amount lost was probably due to the slight instability of the MDA salt.

Extraction efficiency

The average extraction efficiency for six filters spiked at the target concentration is 99.6%.

The stability of extracted and derivatized samples was verified by reanalyzing the above six samples the next day using fresh standards. The average extraction efficiency for the reanalyzed samples is 98.7%.

Recommended air volume and sampling rate

The recommended air volume is 100 L.

The recommended sampling rate is 1 L/min.

Interferences (sampling)

MDI appears to be a positive interference. It was found that when MDI was spiked onto an acid-treated filter, the MDI converted to MDA after air was drawn through it.

Suspected interferences should be reported to the laboratory with submitted samples.

Safety precautions (sampling)

Attach the sampling equipment to the employees so that it will not interfere with work performance or safety.

Follow all safety procedures that apply to the work area being sampled.

Analytical Procedure

Apparatus: The following are required for analysis.

A GC equipped with an electron capture detector. For this evaluation a Tracor 222 Gas Chromatograph equipped with a Nickel 63 High Temperature Electron Capture Detector and a Linearizer was used.

A GC column capable of separating the MDA derivative from the solvent and interferences. A 6 ft X 2 mm ID glass column packed with 3% OV-101 coated on 100/120 Gas Chrom Q was used in this evaluation.

An electronic integrator or some other suitable means of measuring peak areas or heights.

Small resealable vials with Teflon-lined caps capable of holding 4 mL.

A dispenser or pipet for toluene capable of delivering 2.0 mL.

Pipets (or repipets with plastic or Teflon tips) capable of delivering 1 mL for the sodium hydroxide and buffer solutions.

A repipet capable of delivering 25 uL HFAA.

Syringes for preparation of standards and injection of standards and samples into a GC.

Volumetric flasks and pipets to dilute the pure MDA in preparation of standards.

Disposable pipets to transfer the toluene layers after the samples are extracted.

Reagents

0.5 NaOH prepared from reagent grade NaOH.

Toluene, pesticide grade. Burdick and Jackson distilled in glass toluene was used.

Heptafluorobutyric acid anhydride (HFAA). HFAA from Pierce Chemical Company was used.

pH 7.0 phosphate buffer, prepared from 136 g potassium dihydrogen phosphate and 1 L deionized

water. The pH is adjusted to 7.0 with saturated sodium hydroxide solution.

4,4'-Methylenedianiline (MDA), reagent grade.

Standard Preparation

Concentrated stock standards are prepared by diluting pure MDA with toluene. Analytical standards are prepared by injecting uL amounts of diluted stock standards into vials that contain 2.0 mL toluene.

25 uL HFAA are added to each vial and the vials are capped and shaken for 10 seconds.

After 10 min, 1 mL of buffer is added to each vial.

The vials are recapped and shaken for 10 seconds.

After allowing the layers to separate, aliquots of the toluene (upper) layers are removed with a syringe and analyzed by GC.

Analytical standard concentrations should bracket sample concentrations. Thus, if samples fall out of the range of prepared standards, additional standards must be prepared to ascertain detector response.

Sample preparation

The sample filters are received in vials containing deionized water.

1 mL of 0.5N NaOH and 2.0 mL toluene are added to each vial.

The vials are recapped and shaken for 10 min.

After allowing the layers to separate, approximately 1 mL aliquots of the toluene (upper) layers are transferred to separate vials with clean disposable pipets.

The toluene layers are treated and analyzed.

Analysis

GC conditions

Zone temperatures:

Column - 220 degrees C

Injector - 235 degrees C

Detector - 335 degrees C

Gas flows, Ar/CH₄ Column - 28 mL/min(95/5)

Purge - 40 mL/min

Injection volume: 5.0 uL

Column: 6 ft X 1/8 in ID glass, 3% OV-101 on 100/120 Gas Chrom Q

Retention time of MDA derivative: 3.5 min

Chromatogram:

Peak areas or heights are measured by an integrator or other suitable means.

A calibration curve is constructed by plotting response (peak areas or heights) of standard injections versus µg of MDA per sample. Sample concentrations must be bracketed by standards.

Interferences (analytical)

Any compound that gives an electron capture detector response and has the same general retention time as the HFAA derivative of MDA is a potential interference. Suspected interferences reported to the laboratory with submitted samples by the industrial

hygienist must be considered before samples are derivatized.

GC parameters may be changed to possibly circumvent interferences.

Retention time on a single column is not considered proof of chemical identity. Analyte identity should be confirmed by GC/MS if possible.

Calculations

The analyte concentration for samples is obtained from the calibration curve in terms of ug MDA per sample. The extraction efficiency is 100%. If any MDA is found on the blank, that amount is subtracted from

the sample amounts. The air concentrations are calculated using the following formulae.

$\text{ug/m}^3 = (\text{ug MDA per sample}) (1000)/(\text{L of air sampled})$

$\text{ppb} = (\text{ug/m}^3)(24.46)/(198.3) = (\text{ug/m}^3)(0.1233)$
where 24.46 is the molar volume at 25 degrees C and 760 mm Hg

Safety Precautions (analytical)

Avoid skin contact and inhalation of all chemicals.

Restrict the use of all chemicals to a fume hood if possible.

Wear safety glasses and a lab coat at all times while in the lab area.